Arnold Schwarzenegger
Governor

CARBON FOAM-BASED NOx BIOFILER

FEASIBILITY ASSESSMENT AND FINAL EISG REPORT

Prepared For:
California Energy Commission
Energy Innovations Small Grant Program

Prepared By:
University of California, Davis

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Grant No: 00-04

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ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM

INDEPENDENT ASSESSMENT REPORT (IAR)

CARBON FOAM-BASED NO_X BIOFILTER

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PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace. The PIER Program, managed by the California Energy Commission (Commission), annually awards up to $62 million of which 5% is allocated to the Energy Innovation Small Grant (EISG) Program. The EISG Program is administered by the San Diego State University Foundation through the California State University, which is under contract to the Commission.

The EISG Program conducts up to four solicitations a year and awards grants for promising proof-of-concept energy research.

PIER funding efforts are focused on the following seven RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Energy Innovations Small Grant Program
- Energy-Related Environmental Research
- Energy Systems Integration
- Environmentally-Preferred Advanced Generation
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies

The EISG Program Administrator is required by contract to generate and deliver to the Commission an Independent Assessment Report (IAR) on all completed grant projects. The purpose of the IAR is to provide a concise summary and independent assessment of the grant project in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions. The IAR is organized into the following sections:

- Introduction
- Objectives
- Outcomes (relative to objectives)
- Conclusions
- Recommendations
- Benefits to California
- Overall Technology Assessment
- Appendices
  - Appendix A: Final Report (under separate cover)
  - Appendix B: Awardee Rebuttal to Independent Assessment (awardee option)

For more information on the EISG Program or to download a copy of the IAR, please visit the EISG program page on the Commission's Web site at:
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or contact the EISG Program Administrator at (619) 594-1049, or email at:
eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the Commission's Web site at http://www.energy.ca.gov/research/index.html.

Carbon Foam-Based NO_X Bio-filter

EISG Grant # 00-04

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Introduction

The burning of carbon-based fuels is a major source of atmospheric pollution, including oxides of nitrogen (NO_x). Nitrogen oxides can adversely affect human health and degrade the environment. The major drawback of conventional post-combustion, pollution-removal systems is the high cost of treating large volumes of air containing moderate to low concentrations (<100ppm) of NO_x. Many gas-turbine research projects are currently demonstrating NO_x levels of less than 5 ppm (15% O_2) using natural gas fuel and no post-combustion system. These methods employ pre-combustion catalysis or combustion modification. A parallel technology for liquid fuels such as diesel (DF2) or bio-diesel has not yet been demonstrated. A need exists for NO_x reduction techniques that are cost effective and demonstrate high NO_x removal rates when used with liquid or biomass-derived fuels.

Bio-filtration systems are an emerging post-combustion control technology that may be effective in treating gas streams containing NO_x. They are currently used with air streams containing low concentrations of volatile organic compounds and other hazardous air pollutants. Modified bio-filtration methods may permit NO_x removal at a cost of approximately $0.40/lb ($800/ton) in medium to low concentration (<100 ppm) NO_x air streams. Current NO_x removal costs can be as high as $4000/ton. Successful development of a low-cost technology to reduce NO_x concentrations in post-combustion air streams will allow the greater use of alternative fuels by California generators without violating strict air emission standards. Biological treatment of NO_x does not produce additional hazardous by-product streams such as ammonia slip. Successful development of the proposed technology would permit retrofitting.

The researcher proposed a bio-filter based on a new type of rigid carbon foam. The use of this material increased the surface area of the aerobic, autotrophic bio-film with the intention of reducing the residence time. The researcher investigated the role of foam-pore size in reducing both residence time and pore obstruction caused by the bio-film. Bio-films containing chemoautotrophic organisms have demonstrated promise in degrading NO. Previous research has obtained results of 80% NO_x removal and residence times in the bio-filter of approximately 2 minutes. The long residence time may be due to mass-transfer limitation. It is a barrier to the economic feasibility of this technology. The goal of this project was to increase the fraction of NO_x removed while lowering the residence time. The researcher planned to verify the hypothesis that an optimum pore-size, bio-filter packing medium exists and to determine whether the concept would result in a technically and economically feasible bio-filter design.

Bio-filtration tests completed prior to this project showed non-linear NO_x removal for NO_x concentrations above 100 ppm. One of the objectives of this project was to determine if abiotic gas- and liquid-phase oxidation reactions were the mechanisms for the observed non-linearity.

Objectives

The goal of this project was to determine the feasibility of reducing the quantities of NO and NO_2 from flue gas streams using a bio-filtration system based on rigid carbon foam. The researchers established the following project objectives:

1. Design, construct, and test three lab-scale bio-filter columns packed with segments of custom carbon-foam of varying pore dimensions. The objective was to remove 90% of the NO from the gas stream with residence times of less than 2 minutes.
2. Verify that the microbial film removes the more-soluble nitrogen dioxide (NO_2) with equal or greater efficiency than NO.
3. Determine design parameters for scaling a bio-filter to a prototype commercial system.
4. Develop an appropriate packed-bed, mass-transfer model to provide accurate cost estimates for full-scale applications, targeting NO_X removal costs of less than $0.40 /lb.
5. Determine if abiotic NO reactions are an explanation for observed non-linear NO removal efficiency.

Outcomes

1. The researcher constructed and tested three lab-scale bio-filter columns containing rigid carbon foams with 20, 45, and 60 pores per inch (PPI). Overall, the 20 PPI carbon foam exhibited higher removal efficiency and NO_x elimination capacity than the 60 PPI or 45 PPI packing for residence times of 0.6, 1, and 1.5 minutes. NO removal was measured at 35% with residence times near 6 minutes.
2. The researcher did not present conclusive evidence regarding this objective.
3. Efforts to determine design parameters for scaling a bio-filter to a prototype commercial system were discontinued after it became clear that removal efficiencies in a viable range were not feasible.
4. The initial model was based on mass-transfer limited operation and was not designed to handle the complication of gas- and aqueous-phase reaction. The researcher curtailed further model development.
5. The reaction rate estimates indicate that both dry and wet abiotic oxidation of nitric oxide are important processes occurring in the bio-filter, especially when the reaction half-lives are shorter than or near the residence time in the bio-filter.

Conclusions

1. The researcher was not able to achieve high levels of NO reduction or low residence times. Difficulties in executing the experiments may have caused the less-than-anticipated NO removal. Difficulties included maintaining adequate moisture for the medium. The experiments had to be re-started when the medium was allowed to dry out. The lack of robustness of this type of bio-film could be problematic for full-scale commercial operation.

2. The researcher should present conclusive evidence supporting this objective.
3. Long residence times pose a challenge for any equipment intended for commercial use. Size and cost increase with residence time. The researcher should estimate the rate of use of consumables (water, nutrient, etc) per unit of NO removed.
4. The cost of NO_x removal cannot be estimated from the results of this project. The researcher needs to consider several factors, in addition to the cost of the rigid carbon foam. Among these factors are controls, pumps, nutrients, power, and skilled labor.
5. Model development and scale-up of packed-bed bio-filters for NO_x will need to take into account gas-phase and aqueous-phase conversion reactions of NO.

Recommendations

It may still be possible to exploit the ability of biological organisms to rapidly convert nitrite solutions to nitrate aerobically. Questionable experimental practice during the performance of this project may have resulted in the lack of adequate data to support the proof of feasibility. At the conclusion of this project the researcher obtained continuing funds from the California Air Resources Board. In that work the researcher claims to have achieved NO_x removal rates of over 90% with residence times of less than four minutes. With these results, the researcher should evaluate the practicality of a bio-filter using rigid carbon foam for a real application.

Benefits to California

Public benefits derived from PIER research and development are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research, if successful, is reduced environmental impacts of the California electricity supply or transmission or distribution system. However it would serve no purpose to speculate on future public benefits of this project, since the concept feasibility remains unproven.

Overall Technology Transition Assessment

The Program Administrator reviewed the researcher's overall development effort. This includes all activities related to a coordinated development effort, not just the work performed with EISG funds.

Marketing/Connection to the Market

Marketing of this concept has been limited to the publication of technical papers in peer review journals. This is appropriate due to the preliminary nature of this research.

Engineering/Technical

This concept proved neither feasible nor unfeasible. A number of technical challenges must be overcome before a definitive resolution of the feasibility question is within reach.

Legal/Contractual

No patent disclosures were filed as a result of this project.

Environmental, Safety, Risk Assessments/ Quality Plans

Quality plans should be delayed until feasibility has been proven. Quality Plans include Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety and Environmental**.**

Production Readiness/Commercialization

The feasibility of this concept remains unproven. Plans for production or commercialization would be premature and have not been made.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)

Appendix A to IAR 00-04

ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM

EISG FINAL REPORT

Carbon Foam-Based NO_X Biofilter

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Legal Notice

Inquires related to this final report should be directed to the Awardee (see contact information on cover page) or the EISG Program Administrator at (619) 594-1049 or email eisgp@energy.state.ca.us.

Acknowledgement

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Abstract

Three rigid carbon foams of varying pore dimension were evaluated as potential packing materials for aerobic biodegradation of NOx. Mass transfer of NO to the biofilm was hypothesized to be an important limitation in biofilters, and that for sufficiently large pore dimensions, nitrifying biofilms will not obstruct air passages. Hence an optimal pore dimension may exist. Biofilms were developed on the carbon foams by continuous recirculation of a nitrite-containing solution over the packing material prior to their introduction into a packed-column configuration. The rate of conversion from NO_2^--N to NO_3^--N was measured during the biofilm development process. Results of the nitrification rate tests performed after acclimation showed that growth of nitrifying organisms occurred as evidenced by rapid conversion of NO_2^--N to NO_3^--N.

To evaluate the ability of three different pore sizes of carbon foam to support nitrifying biofilms, the liquid-phase nitrifying rate in each biofilter column was measured prior to execution of the gas-phase experiments. The values of nitrite-N elimination capacity show that the biofilter packed with 60 pores per inch (PPI) foam produced the highest initial nitrification rate. The NO removal efficiencies at different inlet NO concentrations and varying empty bed residence times were then measured. In contrast, the gas phase removal efficiency of NO was greatest for the 20 PPI foam packing. Biotic removal efficiencies of about 30% were achieved with a 1.5 minute empty-bed contact time (EBCT) for NO inlet concentrations in the range of 100 to 200 ppm. Non-linear NO removal was observed for NO concentrations above about 100 ppm. The non-constant increase in removal efficiency was attributed to abiotic gas and liquid phase oxidation reactions. The importance of the abiotic reactions requires reassessment of NO removal efficiencies previously reported in the literature. Based upon the current results with autotrophic nitrifying organisms, aerobic nitrification as a method of controlling gas phase NOx using a fixed-bed bioreactor does not appear economic.

Key Words: (nitric oxide, removal efficiency, biofilter, autotrophic, nitrogen oxides)

Executive Summary

Introduction

The burning of fossil fuels is a major source of atmospheric nitrogen oxides (NO_x). Nitrogen oxides can adversely affect human health and be detrimental to the environment. As such, there is considerable interest in the development of efficient, cost-effective technologies to remediate NO_x containing emissions. The major drawback of conventional post-combustion systems is the prohibitive cost of treating large volumes of air containing moderate to low concentrations of NO_x. Biofiltration systems are an emerging post-combustion control technology that may have the potential to be effective treatment alternatives for gas streams contaminated with NO_x since they are suitable for treating low concentration streams. The use of heterotrophic (organisms requiring organic carbon as an energy and carbon source) systems has already been demonstrated (Apel and Turick, 1993; Apel *et al*., 1995; Barnes *et al*., 1994; du Plessis *et al*., 1998; Lee *et al*., 1999; Woertz *et al*., 1998; Chou and Lin, 2000). Heterotrophic systems, however, have the disadvantage of requiring an additional substrate for growth. Chemoautotrophic (organisms are capable of fixing CO_2 for carbon and obtain energy from inorganic substrates, e.g., directly from NO oxidation) have also demonstrated promise in degrading NO (Davidova, 1997; Hudepohl, 1998; Nascimento, 2000). Mass-transfer limitations are believed to have resulted in empty-bed contact times (EBCT - superficial residence time) in the biofilter that would be uneconomic (Nascimento, 2000) though the recent findings of Chou and Lin (2000) appeared highly promising, i.e., 80% removal with an EBCT of approximately 2 minutes. The primary goals of this study were then to:

1) Reduce the cost of NOx removal by biofiltration to approximately $.40/lb in low concentration NOx streams by reducing the residence time requirement with a new type of biofilter packing, a rigid carbon foam with variable pore size.

2) Verify the hypothesis that an optimum pore size biofilter packing medium exists, and determine whether the concept would result in a technically and economically feasible biofilter design.

Project Objectives

In order to accomplish the primary goals described above the following specific project objectives were undertaken:

1) Design and construct three lab-scale biofilter columns and pack them with segments of custom carbon-foam packing of varying pore dimensions. Three sizes were employed so that it would be possible to determine if the pore dimensions of the biofilter packing affected performance.

2) Verify that nitrogen dioxide (NO_2) is removed with equal or greater efficiency than NO by the microbial film. The NO_2 has a greater solubility, but measurements to verify its removal have not been performed. The gas phase removal measurement in the packed

columns would also permit a test of the hypothesis that pore dimension of biofilter packing may have an optimum.

3) Based upon the gas phase removal measurements determine design parameters for scaling a biofilter to a prototype commercial system.

4) Based upon the gas phase removal measurements develop an appropriate packed-bed mass transfer model that can be used to provide accurate cost estimates for full-scale applications.

5) Undertaken a review of the literature and determine if abiotic NO reactions were an explanation for unexpected non-constant concentration dependence of the NO removal efficiency observed.

These five specific objectives were included for the purpose of advancing the state of the technology beyond Stage 3 (Research and Bench Scale Testing) and past Gate 3 (Proof of Feasibility) of the Stages and Gates process.

Project Outcomes

- Task #1 - Evaluation of biofilm development prior to assembling biofilter column

The carbon foams were seeded prior to introduction into the biofilter columns. Results of the nitrification rate tests performed after 50 and 87 days of acclimation. On day 50 a 49% reduction of initial total-N (most or all in the form of NO_2^--N) concentration (116 ppm) was achieved after 12 hours of recirculation over the foam. On day 87 of acclimation, the rate of nitrification was more rapid, with 65% of the initial 204 ppm NO_2^--N being converted to NO_3^-N after 14 hours of recirculation. Growth of nitrifying organisms was indicated by the rapid conversion of NO_2^--N to NO_3^--N. Based upon those conversions, it was determined that the carbon foam sections had active biofilms and were ready to be inserted into the columns.

- Task #1 - Measurement of liquid-phase nitrification rate of different carbon foams in columns

Measurement of the liquid-phase conversion rate of nitrite (NO_2^-) solution by the biofilms on the three different pore sizes of carbon foam in each biofilter were performed prior to execution of the gas-phase experiments. The NO_2^--N elimination capacity demonstrated that the biofilter packed with 60 PPI foam produced the highest nitrifying ability as expected since the 60 PPI carbon foam had the largest specific surface area for biofilm attachment.

- Task #2 and #3 - Removal efficiency and elimination capacity determination of NO

Performance of the biofilter was quantified using removal efficiency and elimination capacity. Removal efficiency is expressed as the difference between the inlet and outlet concentrations normalized by the inlet concentration and is dimensionless. Elimination capacity is expressed as the normalized mass removal per unit time and volume [$g/(m^3 \bullet hr)$]. Difficulties with the liquid distribution system resulted in loss of biologic activity in the columns on two occasions

necessitating re-inoculation of the columns on two separate occasions. Overall, for both sets of measurements the 20 PPI carbon foam exhibited higher removal efficiency and elimination capacity than the 60 PPI or 45 PPI packing for EBCT's of 0.6, 1 and 1.5 minutes. This is in contrast to the column results with nitrite solution where the 60 PPI carbon foam exhibited greater elimination capacity. At a residence time of 6 minutes the differences among the column results were not as distinct although at concentrations ≤ 100 ppm, the 20 PPI column still appeared to have slightly better removal efficiency than either the 60 PPI or 45 PPI columns.. The 60 PPI performed better at concentrations around 300 ppm. We hypothesize that the longer residence time in the columns allowed for greater diffusion into the biomass in the smaller pore size columns. These columns may have had pores that were partially occluded with water trapped in the pores. We believe that the set of three EBCT observations is consistent with the hypothesis of an optimum pore size of packing, rather than simply best performance from the packing with greatest specific surface area.

- Task #5 – Review of literature on abiotic NO reactions and their implications for interpreting the experimental data obtained from Task #2 and #3

An increase of removal efficiency with concentration was observed and reproduced with both sets of experiments performed as part of Tasks #2 and #3. The increase was unexpected and suggested non-linear behavior in the system. At this juncture, a concerted effort was made to understand the non-constant removal efficiency since 1) the implication of the results was that the system behavior was not understood and could not be modeled properly, and 2) economic removal rates would not be achieved aerobically at low concentrations of NO.

The literature review revealed that two reactions could account for the increase in removal efficiency observed in the column tests. The gas phase thermal conversion of nitric oxide, NO, to nitrogen dioxide, NO_2:

$$2NO + O_2 \rightarrow 2NO_2$$

and the overall stoichiometric aqueous phase conversion of NO to NO_2^-:

$$4NO + O_2 + 2H_2O \rightarrow 4H^+ + 4NO_2^-$$

Rate expressions for both reactions are second order in NO concentration and have the following form:

$$d[NO]/dt = - 4k [NO]^2[O_2]$$

Calculations were performed under conditions used in the columns and using rate constant data from the literature. The gas phase conversion was experimentally determined to be within a factor of two of that observed in the column and of similar trend of reaction order. The aqueous phase reaction rate could not be estimated with confidence because of unknown liquid hold-up time in the packing.

The rates estimates indicate that both dry and wet abiotic oxidation of nitric oxide are important processes occurring in the biofilter, especially when the reaction half-lives are shorter than or near the residence time in the biofilter. For biofilters having a residence time on the order of a minute or greater, concentrations as low as about 100 ppm may become significant. Applying a correction for abiotic reaction to the 20 PPI, 1.5 minute EBCT data, the biotic removal efficiency appears to be only between 25 to 35%, slightly improved, but consistent with the range observed by Hudepohl (1998) and Nascimento (2000). Most prior work on biofilters reported in the literature has been for concentrations less than about 100 ppm so that non-constant removal efficiency was not observed or reported. However, the article by Chou and Lin (2000) was conducted at concentrations of about 1000 ppm and EBCT's of about two minutes or longer. Using the above rate expression for gas phase oxidation of NO, approximately half of the removal observed in their experiments could be attributable to abiotic reactions. The consequence is that at the concentration range best suited for biofiltration (< 100 ppm), the removal efficiency for an autotrophic biofilter of packed-bed design is low and the technology uneconomic.

- Tasks #3 and #4 – Terminated further model development and prototype scale-up

The objective of Task #3 was to determine design parameters for scaling a biofilter to a prototype commercial system. Further efforts to determine NO removal profiles for model parameter estimation were not attempted after it became clear that a viable range of removal efficiencies could not be obtained. Similarly, the objective of Task #4 was to develop an appropriate packed-bed mass transfer model that can be used to provide accurate cost estimates for full-scale applications. The model that was initially developed had been based on mass-transfer-limited operation, and was not designed to handle the complication of gas and aqueous phase reaction. Thus further model development was also curtailed.

Conclusions

1) Successful inoculation of the carbon-foam packing was achieved with an aerobic autotrophic biofilm. An initial acclimation period of about two months was required, indicative of the low growth rate of these autotrophic organisms. The organisms were sensitive to drying and re-inoculation and acclimation of at least one month was required before good conversion of nitrite to nitrate was observed. The lack of robustness of this type of biofilm to upset conditions would be problematic for full-scale operation.

2) The higher removal efficiencies observed for the carbon foam packing at high concentrations, i.e., greater than about 100 ppm, appears to be a combination of nitric oxide oxidation in both the gas and aqueous phase by abiotic reactions, and by biotic reaction in the aqueous phase. The higher the concentration, the greater the abiotic contribution.

3) The superior performance of the 20 PPI carbon foam for NO removal at lower residence times, i.e., about one minute, than the higher specific surface area carbon foams (45 PPI and 60 PPI) is consistent with a hypothesis of biofilm

occlusion of small pore spaces. At concentrations less than about 100 ppm, the removal efficiency of all of the carbon foam packings was low. Aerobic biofiltration using autotrophic organisms in a packed-bed configuration does not appear to be a feasible approach for cost-effective NOx control at low concentration.

4) Our analysis of the abiotic reaction literature strongly suggests roughly half of the removal of NO reported in the literature for a fly ash-based biofilter can be attributed to abiotic reaction. The actual biotic removals observed are of a comparable magnitude to that observed in this study. Hence, removal efficiencies in the range of 80% for low NO concentrations are not expected to be achieved in aerobic packed-bed configuration biofilters of economic dimensions.

5) Model development and scale-up of packed-bed biofilters for NOx will need to take into account gas phase and aqueous phase conversion reactions of NO.

Recommendations

It may still be possible to exploit the ability of biological organisms to rapidly convert nitrite solutions to nitrate aerobically. However, the packed-bed configuration using autotrophic bacteria appears to have limitations for mass transfer, and other designs, e.g., membranes in contact with bacterial suspensions may achieve higher transfer rates into the solution phase. Biologically mediated denitrification may still be practicable if an inexpensive energy source for denitrification can be exploited.

Public Benefits to California

An enhanced understanding of the role of abiotic reactions, and autotrophic nitrifier acclimation and susceptibility to drying has resulted. This knowledge will assist other researchers in their efforts to develop biological treatment systems for NOx .

Introduction

The burning of fossil fuels is a major source of atmospheric nitrogen oxides. Nitric oxide (NO) and nitrogen dioxide (NO_2) are the major NO_x components released during combustion processes from both transportation and stationary sources, although, low levels of nitrous oxide (N_2O) can also be emitted (Rasmussen and Khalil, 1986). Typically, 90 to 95 percent of NO_x from combustion emissions is in the form of NO. Nitrogen oxides are pollutants that adversely affect human health and are detrimental to the environment. As such, there is considerable interest in the development of efficient, cost-effective technologies to remediate NO_x containing emissions.

Control of NO_x emissions can be categorized as either pre-combustion, combustion, or post-combustion. Pre-combustion control can be accomplished by reducing the amount of nitrogen introduced into the combustion system, typically in the fuel. Re-design of combustion systems can also lead to a reduction in NO_x emissions, but there is a limit to the feasible reduction that can be achieved. Major advances in pre-mixed and pulsed combustor technology have occurred in recent years that produce NOx levels of 9 ppm or lower for natural gas, but this technologies cannot be applied to all fuels (California Air Resources Board, 2001). Conventional post-combustion controls include selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), adsorption, and scrubbing (absorption). The major drawback of conventional post-combustion systems is the prohibitive cost of treating large volumes of air containing moderate to low concentrations of NO_x. In addition, conventional systems generate secondary wastes, often requiring further treatment.

Biofiltration systems are an emerging post-combustion control technology that may have the potential to be effective treatment alternatives for gas streams contaminated with NO_x. In a biofiltration system, the waste air stream to be treated is passed through a microbially active packed-bed to remove the contaminant. Although biofiltration systems were developed primarily to eliminate odorous contaminants from gases, biofiltration is also applicable to a much wider range of compounds including petrochemicals, solvents, and NO_x emissions (Ottengraf, 1986; Kinney *et al*., 1998; Devinny *et al*., 1999). The use of heterotrophic (organisms requiring organic carbon as an energy and carbon source) systems has already been demonstrated (Apel and Turick, 1993; Apel *et al*., 1995; Barnes *et al*., 1994; du Plessis *et al*., 1998; Lee *et al*., 1999; Woertz *et al*., 1998; Chou and Lin, 2000). Heterotrophic systems, however, have the disadvantage of requiring an additional substrate for growth. Autotrophic systems have also demonstrated promise in degrading NO (Davidova, 1997; Hudepohl, 1998; Nascimento, 2000). Chemoautotrophic organisms are capable of fixing CO_2 for carbon and obtain energy from inorganic substrates. Removal efficiencies up to 70% were achieved without the addition of extraneous carbon sources; however, empty bed residence times of 6-12 minutes were required. Insufficient growth of the autotrophic bacteria and mass-transfer limitations were attributed as the reasons for the long residence times required for NO degradation.

The primary goals of this study were to:

> 1) Reduce the cost of NOx removal by biofiltration to approximately $.40/lb in low concentration NOx streams by reducing the residence time requirement with a new type of biofilter packing.

2) Verify the hypothesis that an optimum pore size biofilter packing medium exists, and determine whether the concept would result in a technically and economically feasible biofilter design.

The remainder of this report is organized in the following way:

- specific objectives are reviewed
- experimental methods are described
- results are presented
- results are discussed in the context of the project objectives
- study conclusions are presented

Project Objectives

In order to accomplish the primary goals described above the following specific project objectives were undertaken:

1) Construct three lab-scale biofilter columns and pack them with segments of custom carbon-foam packing of different pore dimensions (20 PPI, 45 PPI, 60 PPI). Three pore sizes were employed so that it would be possible to determine if the pore dimensions of the biofilter packing resulted in changes in performance.

2) Verify that the more soluble nitrogen dioxide (NO_2) is removed with equal or greater efficiency than NO by the microbial film. Studies up to this point have concentrated on NO removal. The NO_2 has a greater solubility and there is no reason to believe that the microbial films will not also oxidize NO_2 to nitrate, but measurements to verify its removal were to be performed. The gas phase measurements in the packed columns would permit a test of the hypothesis that the pore dimensions of biofilter packing may have an optimum.

3) Determine design parameters for scaling a biofilter to a prototype commercial system. The columns were to be operated under varying conditions of flow rate (residence time) providing data for determination of the length of a transfer unit. Elimination capacity of NO in the columns, *i.e.*, grams of NO removed per unit time per unit volume of reactor, would also be measured in order to determine the normalized capacity of the system to remove NO.

4) Develop an appropriate packed-bed mass transfer model that can be used to provide accurate cost estimates for full-scale applications. Existing packed-bed mass transfer models are based upon correlations with much higher liquid-to-gas ratios than exist in a biofilter (Onda *et al.*, 1960). Design correlations are needed for the lower liquid-to-gas ratios typical of biofilter applications.

5) Undertaken a review of the literature on abiotic NO reactions. Unexpected non-constant concentration dependence of the NO removal efficiency was observed. It was

necessary to determine whether abiotic reactions could contributed significantly to the removal of NO, and whether this was the likely cause of the non-constant concentration dependence observed. Experiments to determine when abiotic reactions became significant were also undertaken so that the abiotic reactions could be taken into account and to understand previous reports of NO removal in the literature.

These five specific objectives were included for the purpose of advancing the state of the technology beyond Stage 3 (Research and Bench Scale Testing) and past Gate 3 (Proof of Feasibility) of the Stages and Gates process.

Project Approach

Experimental methods

The first project objective was accomplished with a biofilter experimental system designed and constructed by Mr. Lance Hershman (Master of Science candidate) and Dr. Jian-meng Chen (collaborator and Visiting Professor). The biofilter system, illustrated in Figure 1, was originally designed to use an ammonia-methane-air burner system that produced NOx. Subsequently, as a result of a laboratory accident involving a concentrated ammonia release, a gas cylinder containing 10,000 ppm of NO was used to replace the burner system. The bulk of the data obtained in this study were obtained with the column configuration shown in Figure 1.

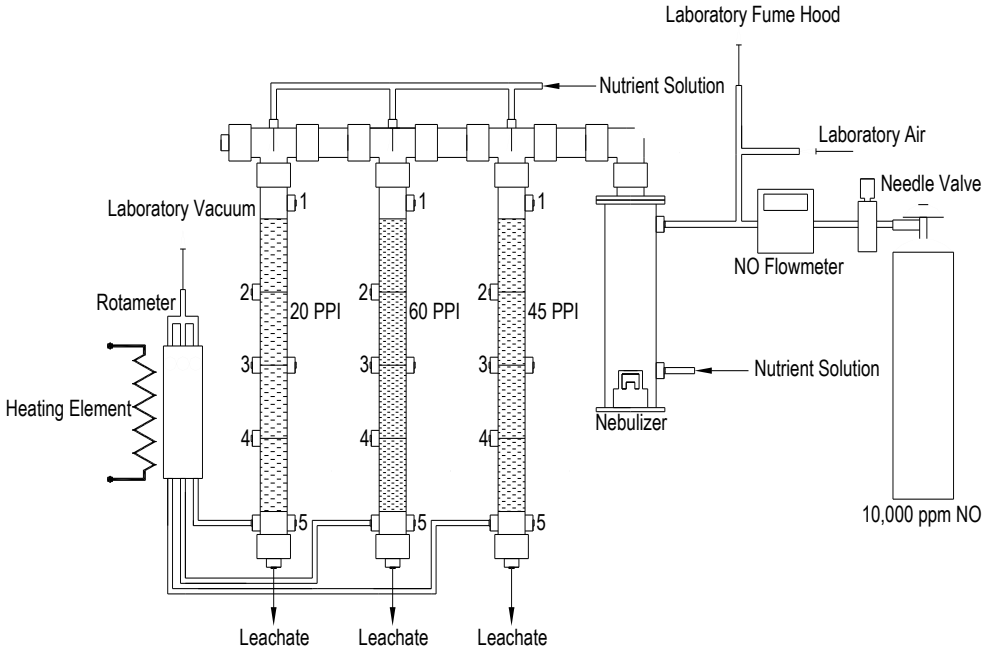

Figure 1. Schematic of Biofilter illustrating three-column configuration with different pore size carbon foam and fed by a single common manifold. In this arrangement, the NOx burner system has been replaced with a tank of NO gas.

The system consisted of three columns that were 2 inches (approximately 5 cm) in diameter and filled to a height of 12 inches with carbon foam packing. The Ultramet carbon foam packing (Ultramet, Pacoima, CA.) is a open-cell silicon carbide material that provides maximum surface area with minimum back-pressure. Three different porosities of carbon foam were selected, 20, 45 and 60 pores per inch (PPI) for use in the biofilter in 3-inch long by 2-inch diameter sections. The specific surface areas for the three porosities were 1175, 2345 and 3655 m^2/m^3. Prior to placement of the Ultrafoam packing into the columns, individual sections were initially inoculated in a basin with autotrophic nitrifying organisms from a previous lava rock nitric oxide removal system (Nascimento, 2000). The NO_2^-N concentrations applied ranged from 10 ppm to 200 ppm and the phosphate (PO_4^{3-}) buffer/trace nutrient solution ranged from 1 to 4 ppm as PO_4^- during the period that the tap water mixture was applied to the carbon foam sections as illustrated in Figure 2A.

Figure 2A. (Left) - Photograph of development of nitrifying biofilm on carbon foam sections illustrating liquid distribution manifold and recirculation bath. Figure 2B. (Right) – Photograph of three identical sections of 60 PPI carbon foam packing placed in the middle column after acclimation of biofilm.

To verify biological activity and prior to undertaking tasks #2 and #3, the nitrification rates of the carbon foam sections were determined after 50 and 87 days of acclimation. Approximately 30 ml samples were collected from the inoculation basin or column leachate for analyses. Samples were filtered using Whatman® (42.5 mm diameter) 0.45 μm glass microfiber filters to remove solids that would interfere with nitrogen measurement. The samples were then immediately analyzed or stored in a freezer at -10°C to avoid further nitrifying activity prior to future measurements. All standards were prepared using deionized water and reagent grade chemicals. Nitrate, ammonia, and nitrite standards were prepared with sodium nitrate ($NaNO_3$), ammonium sulfate ($(NH_4)_2SO_4$), and sodium nitrite ($NaNO_2$), respectively. Total inorganic nitrogen and ammonia nitrogen were measured using a continuous flow conductimetric method (Mansell *et al.*, 2000). The conductimetric analyzer used was the Timberline Model 383 inorganic nitrogen analyzer with the Timberline Model 373 pump diffusion module (Timberline Instruments Inc., Boulder, CO.). The method required a small sample volume of approximately 5 ml. The total inorganic nitrogen concentration was measured by conversion of nitrite (NO_2^-)

and nitrate (NO_3^-) to ammonia (NH_3) using a zinc reduction cartridge. The ammonia concentration was then determined by running the test again without the reduction cartridge. The total oxidized forms of nitrogen (nitrate and/or nitrite) could then be calculated by difference. Photometric analysis of nitrite-nitrogen was performed using an absorbance spectrophotometer (Shimadzu, Model UV160U). Hach NitrVer® 2 nitrite reagent powder pillows were added to 5 ml samples and subsequently analyzed at a wavelength of 585 nm.

To begin tasks #2 and #3, the inoculated packing media were inserted into the biofiltration system after three months of acclimation (Hershman, 2001). Stainless steel braces on the bottom of the last segment supported the carbon foam segments. Leachate was drained at the bottom of each column into tubing connected to a collection bottle. Six 1/8" stainless steel ports were attached to each column at five levels (ports 3A and 3B were on opposite sides of the column at the same level) for nitric oxide sampling. Ports 1 and 5 were used to represent the inlet and outlet concentrations in this nitric oxide study. A spray nozzle (Mist & Cool LLC., Simi Valley, CA.) for the addition of nutrient solution was inserted into a 1 cm hole on the top of gas manifold. A 200 ppm NO_2^-N solution also containing 1 ppm of PO_4^2 was applied to the columns twice an hour for 30 seconds using the spray nozzles. The nutrient solution was introduced into the nozzle using a peristaltic pump (Cole-Parmer, Chicago IL.) attached to a Chrontrol timer system (Hershman, 2001). A pressure regulator and Swagelock needle valve controlled the flow rate of NO from the cylinder through a mass flow meter. The NO was connected by a "tee" to the dilution air supply using 3/8" Teflon tubing. Excess air supply was vented from one leg of the "tee" to an exhaust duct while the nitric oxide/air mixture flowed into the biofilter column through an ultrasonic humidification chamber. The "tee" arrangement allowed the biofilter inlet to remain close to atmospheric pressure. (The pressure in the columns was tested with a Magnehelic pressure gauge capable of measuring –15 to +15 inches of water full scale and found to be at very nearly atmospheric pressure, i.e., less than 0.25 in-H_2O pressure difference). These gas phase studies with NO were conducted by Ms. Kimberly Catton.

The ultrasonic aerosol humidification chamber was an acrylic compartment with nutrient feed inlet, NO/air mixture port. The ultrasonic nebulizer was only operated during the nitrite inoculation period and prior to the first biofilter performance study. It was not used during experiment #1 or #2 subsequently described. The NO/air mixture exited the biofilter columns through a rotameter system connected to the house vacuum. Three rotameters valves were adjusted to control the flow rate out of the biofilter in the range of 0.1 L/min to 1.2 L/min. The rotameters were calibrated prior to placement in the biofilter. A heating pad was wrapped around the rotameter system to reduce condensation.

Six months[1] after the initial inoculation and prior to beginning the gas phase measurements, a nutrient pump line split and the biofilms dehydrated over a weekend. After the drying occurred, conversion from nitrite to nitrate reduced to 0%. Unfortunately, no gas phase removal measurements had been made prior to this event. The biofilm was re-inoculated while the packing remained within the columns with a 500 ml sample of mixed liquor taken from the

[1] The accidental ammonia release with the burner system occurred immediately after inserting the biofilms in the column so that gas phase removal studies could not be undertaken immediately. Subsequent to the installation of the NO gas cylinder supply, the ozone generator in the NOx analyzer also failed and the unit had to be sent to the manufacturer for service resulting in another long delay.

nitrification ditch at the UC Davis Wastewater Treatment Plant. The nitrifying culture at the treatment plant reduced a concentration of 10 mg/L of ammonia to 0.05 mg/L at the plant effluent. Twelve days after the inoculation, the nitrifying culture in the 20 PPI column was reducing 100% of 40 ppm of NO_2^-N, the 60 PPI column was reducing 94% of the 40 ppm of NO_2^-N, and the 45 PPI column was reducing 79% of the 40 ppm of NO_2^-N. An additional spray supplementation of the nitrite and trace nutrients was applied onto the biofilter for approximately 10 hours per week. The concentration of NO_2^-N was raised to 150 ppm and removal increased to 100% in all columns. On the 60th day after re-inoculation, the nitrite feed solution was removed and replaced with water and 1 ppm of dibasic potassium phosphate. For a period of one week gaseous NO (80 ppm) was introduced into the columns continuously at a flow rate of 46 ml/min and an empty bed column residence time of less than one minute. The NO removals at different inlet NO concentrations and varying empty bed residence times were measured on the 2nd, 4th, and 6th day of this experiment and additional measurements extended over a period of three weeks.

The NO gas sample concentrations were measured using a nitrogen oxide analyzer (Monitor Labs Model 8840E). The analyzer was calibrated immediately prior to every testing period using a 48.3 ppm and 100 ppm standard NO calibration gas supplied through its inlet dilution system. Samples were taken from the inlet of each column and the outlet of each column after the reading stabilized and held for at least one minute. A waiting period of five times the column residence time was maintained prior to making measurements after any adjustments to the NO concentration or residence time of the system. Data from those measurements are referred to as the "first 3-week experiment."

Another pump failure and drying event occurred over a weekend and reduced the biofilters' removal to zero. A second re-inoculation was performed. The same nutrient solution was provided only via the nozzle spray, without using the ultrasonic humidification system, for a period of two months before making the gas measurements that constituted the "second experiment." The second NO removal experiment was conducted over a period of four weeks of continuous NO addition at approximately 80 ppm. Data were collected once a week at several different empty bed residence times and concentrations. After the "second experiment" the biofilm was dehydrated and abiotic oxidation tests were performed at the different residence times used during the "first" and "second" experiments.

The first set of NO removal experiments provided a dataset with unexpected trends in removal efficiency as a function of concentration. Task #2 to conduct experiments of nitrogen dioxide (NO_2) removal were not undertaken, in favor of a careful examination of the NO measurement methodology and repeat of the first set of experimental runs. It became clear that the non-linear behavior of the system as NO concentration increased required addition of another task #5 to review the literature on abiotic reactions of NO and NO_2 in the gas and aqueous phase.

Literature review on abiotic reactions of NO

There has been no mention of the influence or significance of abiotic NO reactions in the biofilter literature, prior to the current study and it was not anticipated to play a significant role. However, many abiotic nitric oxide reactions occur in the atmosphere and in the aqueous phase.

At the concentrations of NO present in the ambient environment, these are generally slow unless photochemically driven. Nevertheless, as discussed in the Project Outcomes, the thermal oxidation reactions of NO have a second order dependence on concentration. Because of the non-constant concentration dependence of NO removal efficiency data observed from the columns, abiotic reactions were suspected of having a possible role and were reviewed as a new Task #5.

The problems and delays that occurred in maintaining an active biofilm, the low removal efficiencies observed, and the determination that abiotic reactions may have contributed to promising results reported in the literature, led us to abandon Task #3 and curtail further work on Task #4. It became clear that a commercially viable aerobic autotrophic fixed-film NOx biofilter would not be practicable. Efforts to examine the viability of a heterotrophic NOx biofilter continue even as this report is written under a supplemental Air Resources Board contract #00-311.

Project Outcomes

- Task #1 - Evaluation of biofilm development prior to assembling biofilter column

The nitrification rate (conversion from NO_2^--N to NO_3^--N) was measured during the biofilm development process. On the 50^{th} and 87^{th} day after inoculation, samples were taken from the recirculation solution at 2-hour intervals over a 24-hour period after the renewal of the nutrient solution. The changes in NO_2^--N and total-N concentrations with time were obtained. Results of the nitrification rate tests performed after 50 and 87 days of acclimation are displayed in Figure 3 below. The 50-day acclimation test showed an initial total-N (most or all in the form of NO_2^--N) concentration of 116 ppm. After twelve hours, the NO_2^--N concentration was reduced by 49%. Little or no ammonia was detected in the samples, suggesting all NO_2^--N was oxidized to NO_3^-N. After 87 days of acclimation, the rate of nitrification was more rapid. After 14 hours, 65% of the initial 204 ppm NO_2^--N was converted to NO_3^--N. Growth of nitrifying organisms was indicated by the rapid conversion of NO_2^--N to NO_3^--N. Based upon those conversions, it was determined that the carbon foam sections had active biofilms and were ready to be inserted into the columns.

In order to evaluate differences in the nitrifying ability of the three different pore sizes of carbon foam, the liquid-phase nitrifying rate in each biofilter column was measured prior to execution of the gas-phase experiment. The values of NO_2^--N elimination capacity show that the biofilter packed with 60 PPI foam produced the highest nitrifying ability. The 60 PPI carbon foam had the largest specific surface area for biofilm attachment.

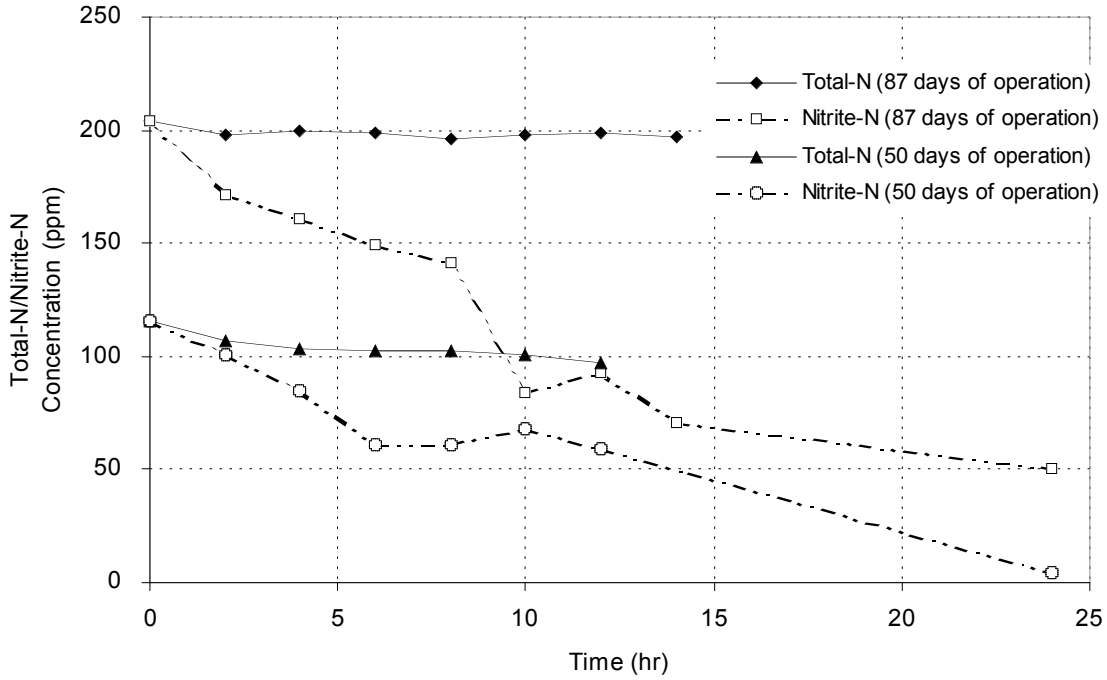

Figure 3. Total-N and Nitrite-N concentrations in column leachate as a function of time after 50 and 87 days of acclimation.

- Task #1 - Measurement of liquid-phase nitrification rate of different carbon foams in columns

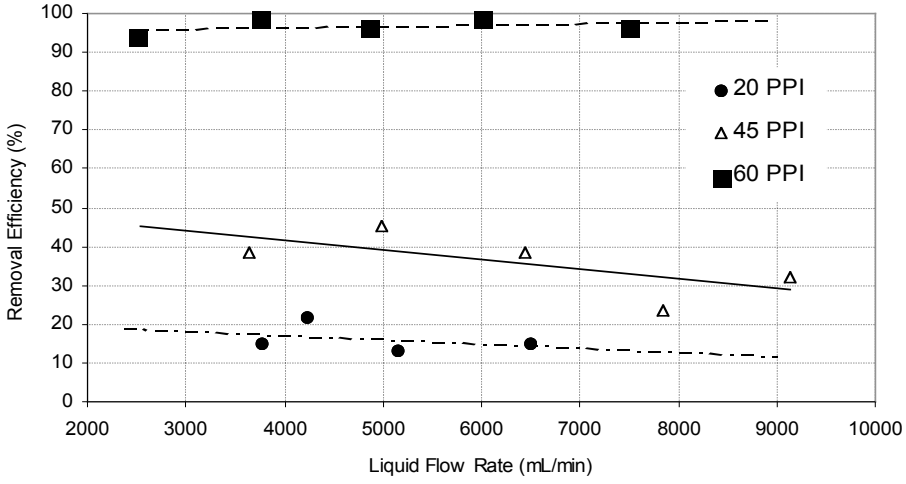

Figure 4. Initial NO_2^--N removal efficiency when carbon foam sections were inserted into the columns.

- Task #2 and #3 - Removal efficiency and elimination capacity determination of NO

Performance of the biofilter was quantified using removal efficiency and elimination capacity. Removal efficiency is derived using the following equation:

$$Efficiency = \frac{(C_1 - C_5)}{C_1} \times 100\% .$$

C_1 = Initial gas phase concentration [ppm] of NO at port 1 of each column

C_5 = Gas phase concentration [ppm] at the end of the column at port 5 of each column

Elimination capacity was calculated by converting the concentration of gas into a mean, mass-based removal quantity normalized per volume of packing material and per time unit. Plotting elimination capacity versus mass loading rate enabled all three EBCT and varied concentrations to be plotted on one graph. The elimination capacity was computed from the measured data as:

$$\text{Elimination Capacity} = \frac{(C_1 - C_5) \cdot MW}{24.95 \cdot 1000 \cdot \left(EBCT / 60\right)}.$$

Elimination capacity is expressed as the normalized mass removal per unit time and volume [g/(m^3•hr)], where,

EBCT is the empty-bed contact time in expressed in units of [min]

MW is the molecular weight of nitric oxide, 30 [g/g-mol)]

C_i is concentration at the sample port "i" expressed in units of [ppm]

Results of gaseous NO removal at varying inlet concentrations and NO residence times of 0.6 to 1.0 minutes from the first 3-week experiment are presented in Figure 5.

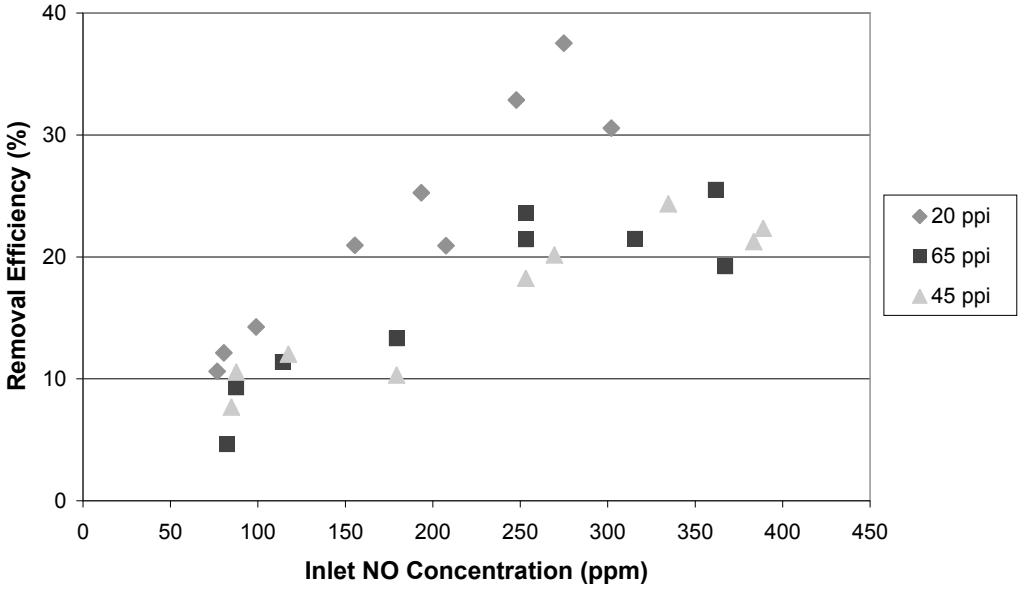

Figure 5. NO removal at residence times ranging from 0.6 to 1.0 minutes during the 1st experiment after 3-week acclimation.

Overall, the 20 PPI carbon foam exhibited higher removal efficiency than the 60 PPI or 45 PPI packing, in contrast to the column results with NO_2^- solution. The best removal for the 20 PPI was apparently 37% at an inlet concentration of nearly 300 ppm of NO, and the lowest removal efficiency was 7% at less than 100 ppm.

The gas flow rate through the columns was decreased to increase the empty-bed contact time (EBCT) and another set of NO removal data were obtained for a 1.5-minute EBCT as shown in Figure 6.

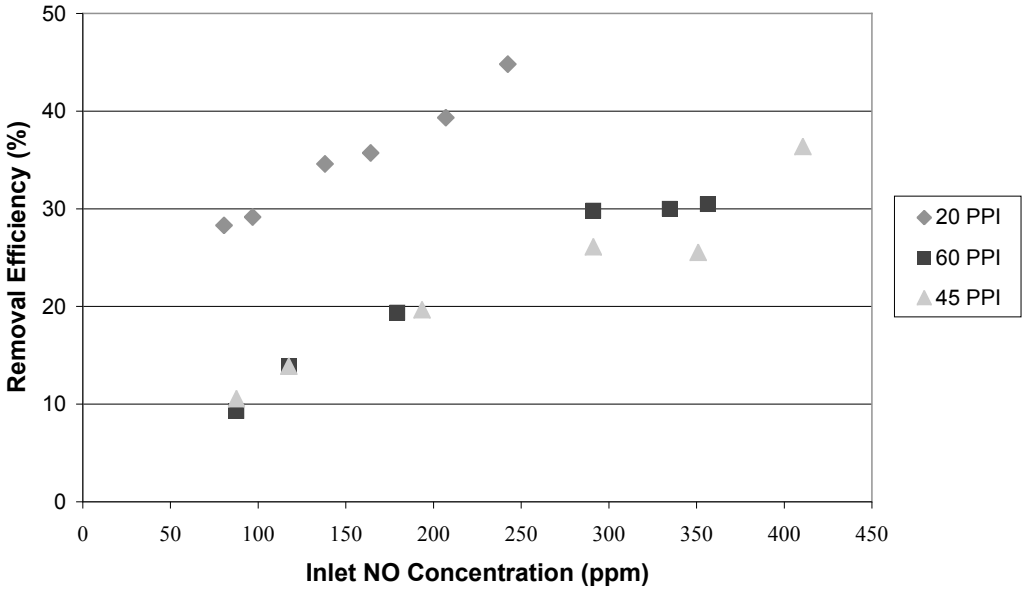

Figure 6. NO Removal at a residence time of 1.5 minutes during the 1st experiment after 3-week acclimation.

Once again, the 20 PPI foam-filled column appeared to exhibit consistently higher removal efficiencies as a function of increasing inlet NO concentration, while those of the 60 PPI and 45 PPI foams were similar, but considerably lower. The highest removal efficiency achieved by the 20 PPPI foam was 45% at 250 ppm.

The EBCT was increased to 6 minutes and results are shown in Figure 7. The differences among the column results were not as clear in this test although at the lowest concentrations applied, the 20 PPI column still appeared to have slightly better removal efficiency than either the 60 PPI or 45 PPI columns.. The 60 PPI performed better at concentrations around 300 ppm with 57% removal. High NO concentrations could not be achieved at the inlet of the 20 PPI column for reasons that were not initially understood. The 20 PPI column was placed furthest from the NO source, and as determined later, that resulted in a substantially longer residence time in the inlet manifold at low flow rates (long residence times). The long residence time in the inlet manifold allowed more gas phase conversion of NO to NO_2, especially as concentration increased. Thus the inability to achieve higher NO concentrations at the inlet of the 20 PPI column is attributed to losses in the inlet manifold due primarily to abiotic reaction. We hypothesize that the longer residence time in the columns allowed for more time for diffusion into the biomass in the smaller pore size columns. These columns may have had pores that were partially occluded with water trapped in the pores. We believe that set of three EBCT observations is consistent with the hypothesis of an optimum pore size of packing, rather than best performance from the packing with greatest specific surface area.

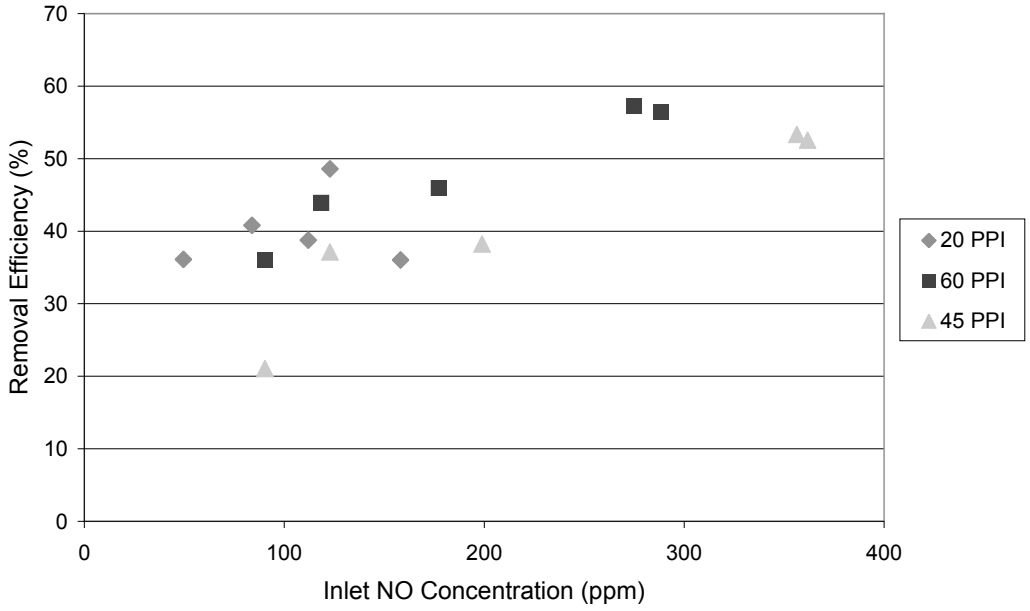

Figure 7. NO removal at a residence time of 6 minutes during the 1st experiment after 3-week acclimation.

The results of all three experiments are plotted on one graph as elimination capacity in Figure 8. The solid straight line in Figure 8 represents 100% removal efficiency. None of the columns at the various residence times achieved 100% removal. The 20 PPI column at the 0.6 to 1.0-minute and the 1.5-minute EBCT had the highest elimination capacities, while the 45 and 60 PPI columns had greater elimination capacity, i.e., performed better, at a 6-minute EBCT. A careful examination of the 20 PPI removal efficiency data suggests that column performance began to fail at successively lower concentrations for longer residence times. Based upon the abiotic reaction literature review, we hypothesize that the increasing oxidation of NO to NO_2 occurred in the inlet manifold with increasing EBCT and subsequent formation of nitrous and nitric acid may have inhibited the autotrophic organisms. Davidova et al. (1997) observed pH sensitivity below about pH 6.0.

A second set of experiments was conducted under as nearly identical conditions as possible two months[2] after the 1st experiment. The primary purpose of the second set of experiments was to verify that the unexpected increase in removal efficiency with concentration was not a sampling artifact. Prior to the 2nd experiment the NOx analyzer was examined to eliminate sampling artifacts as a cause for the observations. The aqueous NO_2^- removal through the columns was not quite as high as before the first set of experiments, thus the biofilms in the columns may not have been as robust as before. Flow rate was set to produce an EBCT of about 0.6 minutes and the results are plotted in Figure 9.

[2] A second tubing pump line "split" over a weekend between the first and second experiments resulting in drying of the biofilms. Re-seeding and acclimation of the columns was necessary.

Removal efficiency again increased with increasing NO concentration. The 20 PPI performed the best at the low residence time, but the differences between the different pore sizes is less than in the first experiment. One data point for the 45 PPI column and one data point for the 20 PPI column appear anomalous, and were most likely the result of experimental error such as insufficient time between samples after adjusting concentrations. The consistently better performance of the 20 PPI packed column is indicative that the packing with the largest specific interfacial area for biofilm growth does not necessarily translate into the highest performance in terms of NO removal.

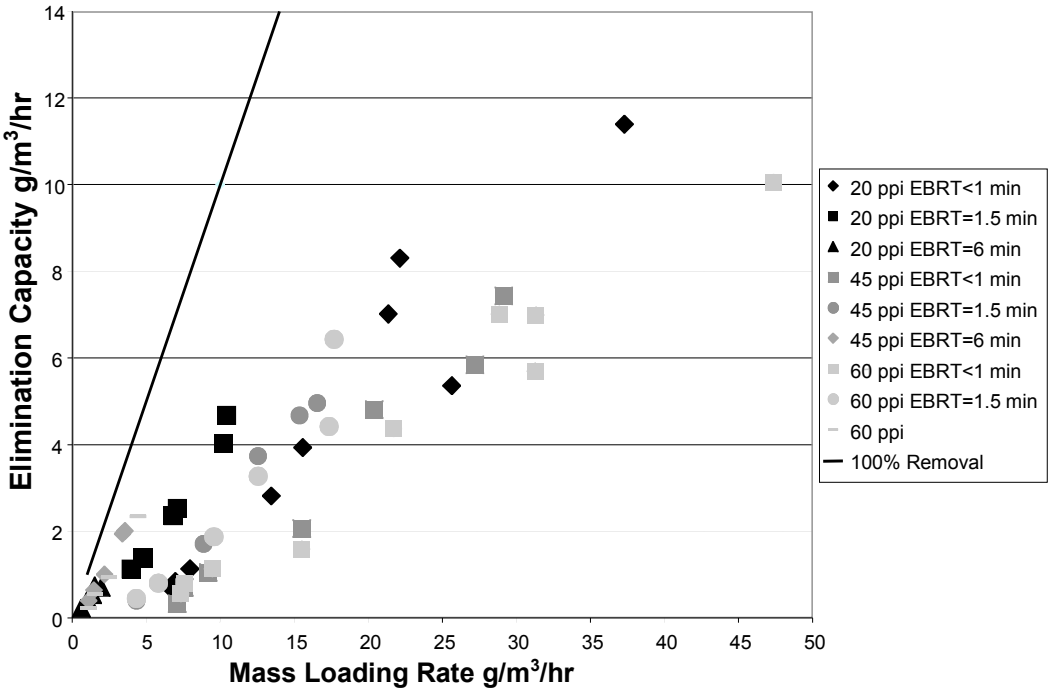

Figure 8. NO elimination capacity for each column at each residence time during the 1st experiment after 3 week acclimation.

Consistent with the first set of experiments, the 20 PPI column performance appeared to drop at the highest concentration applied (about 450 ppm). The same pattern was observed for a 2-minute EBCT and a 6-minute EBCT but at successively lower NO concentrations. The drop-off in concentration, as noted earlier is attributed to inhibition of biological activity resulting from a drop in the pH of the aqueous phase in the column as nitrous and nitric acid were formed.

A summary plot of elimination capacity is shown in Figure 10. Overall elimination capacities were of a similar magnitude but slightly lower than observed in the first experiment. The data exhibited more scatter as well. The second re-seeding of the column, after it dried out, apparently was not as successful as the first re-seeding. Nevertheless the non-constant increase of removal efficiency with concentration was reproduced. At this juncture, a concerted effort was made to understand the non-constant removal efficiency since 1) the implication of the results was that the system behavior was not understood and could not be modeled properly, and 2) economic removal rates would not be achieved aerobically at low concentrations of NO.

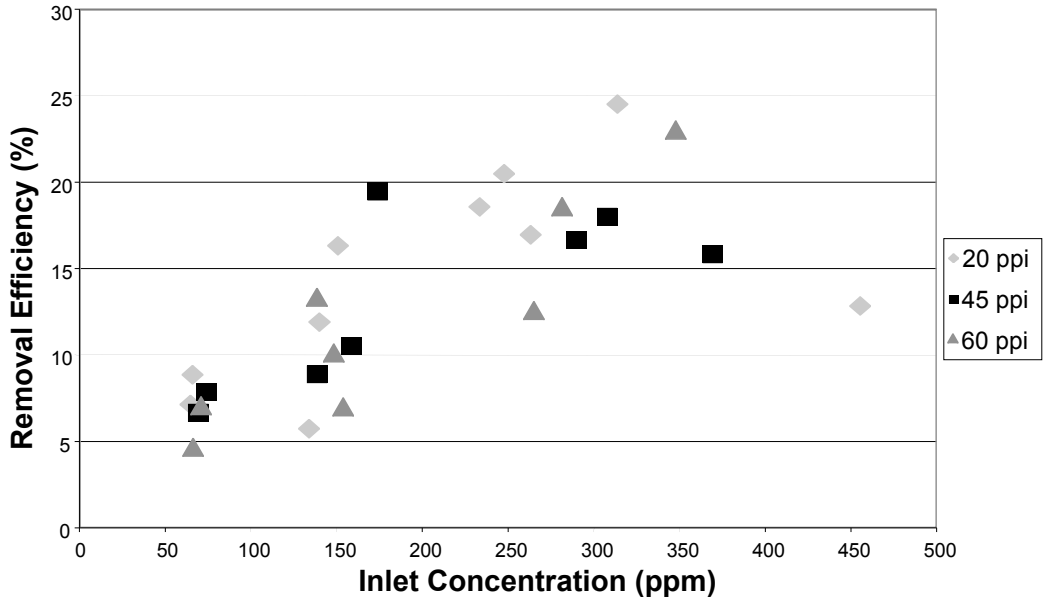

Figure 9. NO removal at residence time of 0.6 minutes during the 2nd experiment of 4-week acclimation.

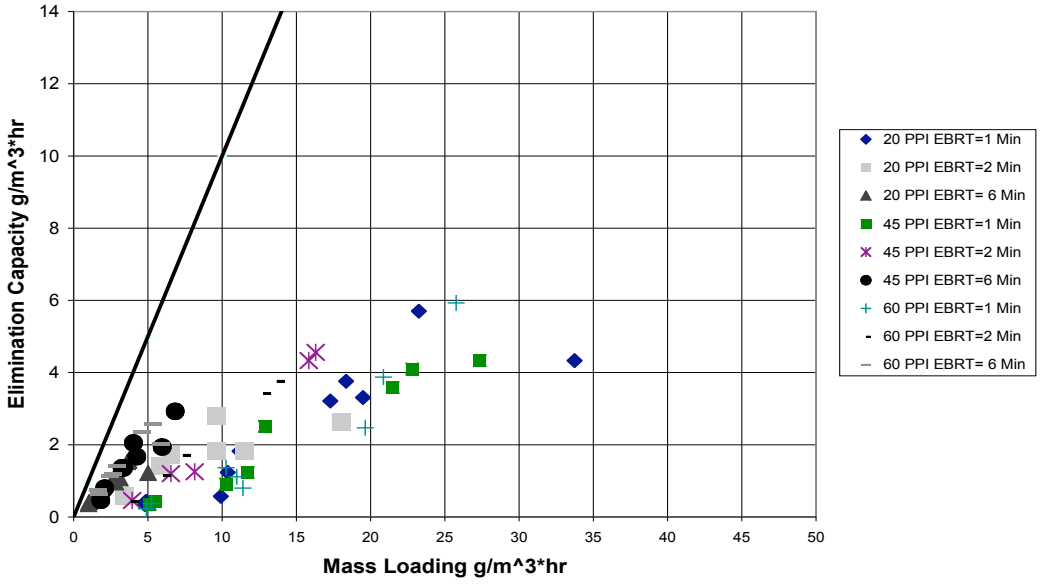

Figure 10. NO elimination capacity for each column at each residence time for the 2nd experiment after 4-week acclimation.

- Task #5 – Review of literature on abiotic NO reactions and their implications for interpreting the experimental data obtained from Task #2 and #3

The gas phase thermal conversion of nitric oxide, NO, to nitrogen dioxide, NO_2, is given in equation 1.

$$2NO + O_2 \rightarrow 2NO_2 \quad (1)$$

The rate expression for the oxidation of nitric oxide to nitrogen dioxide is a second order relationship that is given in equation 2.

$$d[NO]/dt = -2k\,[NO]^2[O_2] \quad (2)$$

The rate constant k is equal to $k = 1.066 \text{ X } 10^{-5}/T^2 * \exp(530/T)$ ppm^{-2} min^{-1} (Seinfeld, 1986). In the presence of oxygen, the rate of conversion of nitric oxide to nitrogen dioxide increases as the square of concentration. In a typical aerobic biofilter the oxygen concentration would be essentially constant at about 210,000 ppm.

The overall stoichiometric aqueous phase conversion of NO to NO_2^- is shown in equation 3.

$$4NO + O_2 + 2H_2O \rightarrow 4H^+ + 4NO_2^- \quad (3)$$

The rate expression for aqueous phase oxidation of nitric oxide has been quantified in equation 4.

$$d[NO]/dT = -4k_{aq}\,[NO]^2[O_2] \quad (4)$$

Clearly this is not an elementary reaction. Although the exact mechanism is uncertain, the following reactions appear to explain the kinetic studies that have been performed (Awad and Stanbury, 1993; Pires et al., 1994):

$$2NO + O_2 \rightarrow 2NO_2 \quad (5)$$

followed by the two rapid reactions:

$$NO + NO_2 \rightarrow N_2O_3 \quad (6)$$

$$N_2O_3 + H_2O \rightarrow 2NO_2^- + 2H^+ \quad (7)$$

The value of the rate constant k_{aq} in equation 4 varies with the source as cited by several different researchers. Pogrebnaya et al. (1975) derived $4k_{aq} = 9 \text{ x} 10^6$ $M^{-2}s^{-1}$, Wink et al. (1993) found that $4k_{aq} = 6 \pm 1.5 \text{ x } 10^6$ $M^{-2}s^{-1}$ and Awad and Stanbury (1993) obtained that $4k_{aq} = 8 \text{ x } 10^6$ $M^{-2}s^{-1}$. There is a corresponding reaction in the gas phase to reaction 7 that involves NO, NO_2,, and water to form nitrous acid:

$$NO + NO_2 + H_2O \rightarrow 2\,HNO_2 \quad (8)$$

Calculations of the rate of gas-phase formation of nitrous acid (equation 8) at the concentrations of NO, NO_2 and saturated air used in this study, show that it is too slow to be significant.

The rate expressions above indicate that both dry and wet abiotic oxidation of nitric oxide are important processes occurring in the biofilter especially when the reaction half-lives are shorter than or near the residence time in the biofilter. For biofilters having a residence time on the order of a minute or greater, concentrations as low as about 100 ppm may become significant as illustrated in Figure 10 below for abiotic gas phase reaction. Several of the abiotic reactions described above, (1) and (3) likely contributed to the experimental removal efficiencies observed when concentration was increased above about 100 ppm in the column studies. Abiotic wet removal could not be estimated accurately because the liquid hold-up time by the carbon foam column packings were unknown.

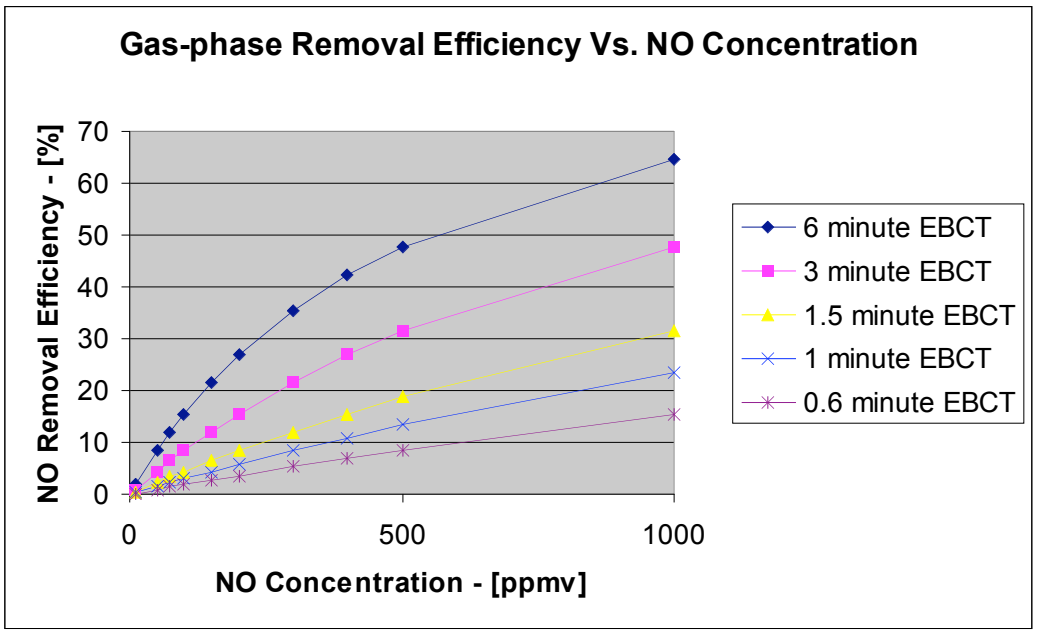

Figure 11. Estimated abiotic gas-phase NO removal efficiency (Eq. 2) for various empty-bed contact times (EBCT) as a function of column inlet concentration.

Task #5 – Abiotic biofilter column tests

Abiotic experiments were performed at a concentration of 150 ppm to verify the hypothesis that abiotic oxidation in the biofilter was taking place. The abiotic tests were first conducted with dry biofilter conditions to quantify gas-phase oxidation, and again with a wet biofilter (the biofilm was allowed to die) to establish removal from both the aqueous and gas phases. The results of the 150 ppm abiotic wet and dry experiment are plotted against the theoretical gas-phase removal based on the kinetics of nitric oxide oxidation (equation 1) in Figure 12. The results are only shown for the 20 PPI column because the trends and results were similar for all three columns.

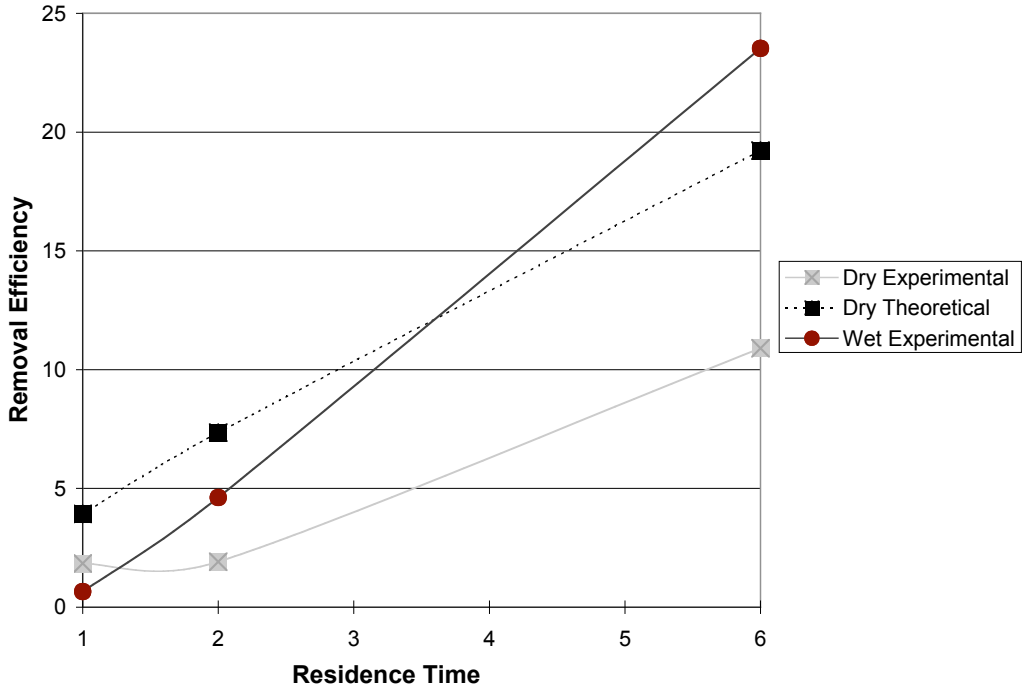

Figure 12. Dry and wet experimental removal of NO compared to gas-phase dry removal estimated by the rate expression in equation 2 for 150 ppm initial NO concentration and varying residence times (empty-bed contact time).

As residence time increased to 6 minutes, dry NO removal increased to nearly 12%, and to about 24% for wet removal. Significant abiotic aqueous phase oxidation appears to have caused an increase in removal as well. However, theoretical aqueous phase oxidation was not calculated because several parameters including wetted surface area and liquid hold-up time were not known. Based on the data for the 20 PPI column, approximately half of the NO removal observed with the biofilm present in the first and second experiments was abiotic.

The calculated gas phase removal efficiency based on the literature rate constant value appears to be greater than the experimental gas phase removal by a factor of 2, but the trend is similar. Non-plug flow conditions through the column may be a reason that the calculated and measured removals do not coincide. In Figure13, the experimental data from the first experiment were corrected using only the theoretical gas-phase abiotic oxidation of nitric oxide. The theoretical gas-phase oxidation was chosen to correct the data because a correction could then be computed at each concentration used in the first experiment. This may lead to an over-correction of the actual removal because the data in Figure 12 suggest that the calculated dry gas phase removal efficiencies are twice that of dry gas phase experimental measurements. However, because the wet column experimental data are greater than the dry experimental removals, the estimated correction may be closer.

It should be noted that the longer gas phase residence time in the columns correspond to lower total flow rate in the gas supply manifold and results in a greater manifold residence time, particularly for the 20 PPI column which was farthest from the NO source. More conversion of

NO to NO_2 probably occurred prior to entering the 20 PPI column compared to the 60 and 45 PPI columns. Thus the abiotic aqueous reaction rate may be higher in the 20 PPI column at longer manifold residence times since the additional fast reactions shown in equations (6) and (7) would occur, and NO_2 is about 10 times more soluble in water than NO. This would effectively increase the mass transfer rate of NO to the aqueous phase since the concentration gradient in the solution phase would be greater.

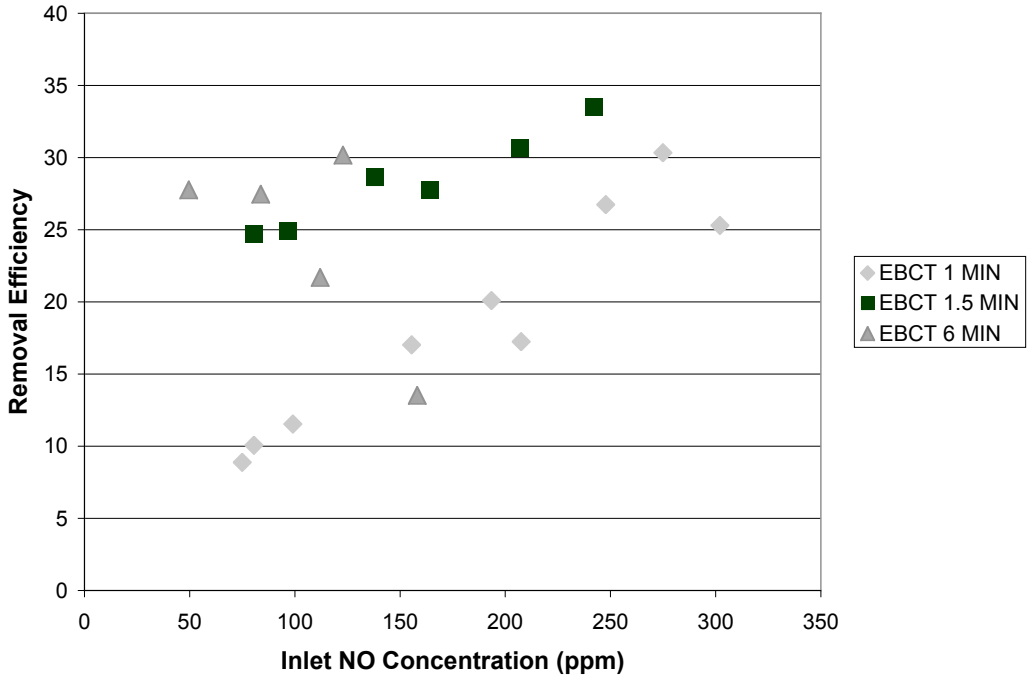

Figure 13. Removal efficiency from the first experiment corrected for abiotic removal in the 20 PPI column.

After correcting for the gas-phase calculated abiotic reaction rate the 1.5-minute EBCT time had the greatest biotic removal and appeared to be between 25 to 35%. That performance is an improvement over our best previous results (Hudepohl, 1998), but is far from being economic for full-scale application of a fixed-film biofilter of this design. The second experiment's corrected data set yielded a maximum removal efficiency of about 25% at a 6-minute residence time and concentration of 100 ppm, considerably less than the first experiment, indicative that the biofilm in the second experiment was not as robust. We conclude that abiotic oxidation probably accounted for the increased removal efficiency observed as concentration increased.

The original hypothesis for this study was that NO removal was mass-transfer limited because of biofilm growth that covered or partially occluded the internal pores of the high surface area media (glass Siran rings) that had previously been used (Davidova, 1997). When applying gaseous NO, the 20 PPI foam had superior removal, particularly at the higher flow rates (shorter EBCT) suggesting that by the time the foam had been re-seeded, some blockage of the smaller pores of the 60 and 45 PPI foam had occurred. The difference in performance appeared to be proportionately less at longer EBCT, which would be consistent with greater time available for

diffusion into occluded or partially occluded pores. We hypothesize that greater channeling occurred in the 60 PPI column, and that at longer residence time, more NO diffuses into partially occluded portions of the 60 PPI foam. Channeling could be occurring to varying degrees in the different pore size columns and as concentration increases, a greater proportion of the NO is able to diffuse into active biomass for removal.

Previous work by Chou and Lin (2000) whose data (≈80% removal efficiency) are based on concentrations as high as about 1200 ppm and 2 minutes EBCT were probably not solely the result of biological removal, but simply a combination of abiotic reaction with some biological activity. (They indicate that their method of NO generation also resulted in an initial NO_2 concentration of about 1% further speeding the abiotic reactions.) Figure 14 adapted from their paper illustrates the time course of NO removal in their fly ash packed-bed reactor. Application of the dry gas rate expression for NO oxidation under those conditions, i.e., 1200 ppm and 2-minute residence predicts that 40% of the removal would be by gas-phase conversion of NO to NO_2 alone. Correcting for that amount, the range of biotic removal observed in the Chou and Lin study would only be about 30 to 40%, approximately the same range we observed.

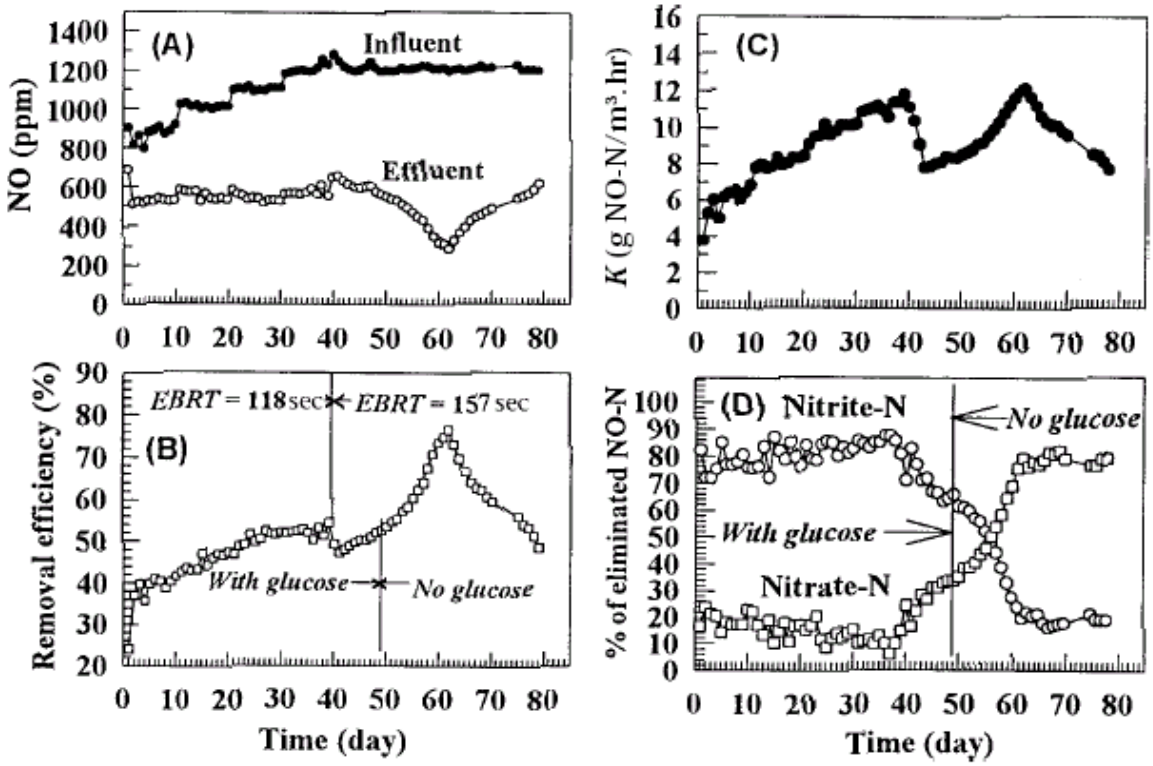

Figure 14. Adapted from Chou and Lin (2000) illustrating their removal efficiency from a fly ash based packed column. Note the initial removal efficiency (panel lower right) observed even before the biofilter had time to acclimate to the introduction of NO and the initial appearance of nitrite-N (lower left). Conversion of the nitrite to nitrate did not occur until approximately 40 days of operation and acclimation.

Biofiltration is a low cost technology applicable to low to moderate concentrations of pollutants of VOCs and other soluble compounds. In the case of natural gas turbines the current California emission standard is 9 ppm. At 100 ppm, 90% removal efficiency is required to meet that standard. At 25 ppm, only about 70% removal efficiency is needed. Nevertheless, the biofilter columns in these experiments did not achieve 90% efficiency at 100 ppm nor even 70% efficiency at 25 ppm, at the concentrations and residence times applied (up to 6 minutes) with or without abiotic reaction.

At this stage the evidence strongly suggests that aerobic biofiltration of NOx with a fixed bed biofilter does not appear to be commercially feasible for industrial purposes at the lower concentration range, i.e., about 100 ppm or less that was the target range for this technology.

- Tasks #4 – Terminated further model development and prototype scale-up

The objective of Task #3 was to determine design parameters for scaling a biofilter to a prototype commercial system. Further efforts to determine NO removal profiles for model parameter estimation were not attempted after it became clear that a viable range of removal efficiencies could not be obtained. Similarly, the objective of Task #4 was to develop an appropriate packed-bed mass transfer model that can be used to provide accurate cost estimates for full-scale applications. The model that was initially developed had been based on mass-transfer-limited operation and was not designed to handle the complication of gas and aqueous phase reaction. Thus further model development was also curtailed.

Conclusions

1) Successful inoculation of the carbon-foam packing was achieved with an aerobic autotrophic biofilm. An initial acclimation period of about two months was required, indicative of the low growth rate of these autotrophic organisms. The organisms were sensitive to drying and re-inoculation, and acclimation of at least one month was required before good conversion of nitrite to nitrate was observed. The lack of robustness of this type of biofilm to upset conditions would be problematic for full-scale operation.

2) The higher removal efficiencies observed for the carbon foam packing at high concentrations, i.e., greater than about 100 ppm, appears to be a combination of NO oxidation in both the gas and aqueous phase by abiotic reactions, and by biotic reaction in the aqueous phase. The higher the concentration, the greater the abiotic contribution.

3) The superior performance of the 20 PPI carbon foam for NO removal at lower residence times, i.e., about one minute, than the higher specific surface area carbon foams (45 PPI and 60 PPI) is consistent with a hypothesis of water or biofilm occlusion of small pore spaces. At concentrations less than about 100 ppm, the removal efficiency of all of the carbon foam packings was low. Aerobic biofiltration using autotrophic organisms in a packed-bed configuration does not

appear to be a feasible approach for cost-effective NOx control at low concentration.

4) Our analysis of the abiotic reaction literature strongly suggests roughly half of the removal of NO reported in the literature for a fly ash-based biofilter can be attributed to abiotic reaction. The actual biotic removals observed are of a comparable magnitude to that observed in this study. Hence, removal efficiencies in the range of 80% for low NO concentrations are not expected to be achieved in aerobic packed-bed configuration biofilters.

5) Model development and scale-up of packed-bed biofilters for NOx will need to take into account gas phase and aqueous phase conversion reactions of NO.

Recommendations

It may still be possible to exploit the ability of biological organisms to rapidly convert nitrite solutions to nitrate aerobically. Abiotic reactions that convert NO to NO_2 and nitrite are not necessarily detrimental since NO_2 has a Henry's coefficient about an order of magnitude lower (more soluble) than NO, and formation of nitrite is rapid through reaction of NO and NO_2 to form NO_2^- in the aqueous phase. Since efficient conversion of nitrite to nitrate has been demonstrated by passing liquid over the carbon foam packing, removal of the nitrite would regenerate the packing. However, based upon this and previous studies of NO removal in the literature, the packed-bed configuration using autotrophic bacteria appears to have limitations for mass transfer, and other designs, e.g., membranes in contact with bacterial suspensions may achieve higher transfer rates into the solution phase. Biologically mediated denitrification also shows promise.

Public Benefits to California

An enhanced understanding of the role of abiotic reactions and autotrophic nitrifier acclimation and susceptibility to drying has resulted. This knowledge will assist other researchers in their efforts to develop biological treatment systems for NOx.

References

Apel, W.A. and Turick, C.E. (1993). "The Use of Denitrifying Bacteria for the Removal of Nitrogen Oxides from Combustion Gases." *Fuel*. 72:1715-1718.

Apel, W., Barnes, J. and Barrett, K. (1995). "Biofiltration of Nitric Oxide from Fuel Combustion Gas Streams." Proc. Air and Waste Management Association 88th Annual Meeting & Exhibition, San Antonio, Texas, June 18-23.

Awad, H.H. and Stanbury, D.M. (1993). "Autooxidation of NO in Aqueous Solution." *International Journal of Chemical Kinetics*, Vol. 25, 375-381.

Barnes, J.M., Apel, W.A., and Barrett, K.B. (1994). "Removal of Nitrogen Oxides from Gas Streams Using Biofiltration." *Journal of Hazardous Materials*. 41(2):315-326.

California Air Resources Board (2001). Technology briefs posted at the Innovative Clean Air Technology Program. www.arb.ca.gov/research/icat/projects.htm.

Chou, M. and Lin, J. (2000). "Biotrickling Filtration of Nitric Oxide." *Journal of Air and Waste Management Association*. 50:502-508.

Davidova, Y., Schroeder E.D., Chang D.P.Y. (1997). "Biofiltration of Nitric Oxide", Paper 97-WP71B.05, CD-ROM Proc. Air & Waste Management Association 90th Annual Meeting & Exhibition, Toronto, Canada, June 8-13.

du Plessis, C.A., Kinney, K.A., Schroeder, E.D., Chang, D.P.Y., Scow, K.M. (1998). "Denitrification and nitric oxide reduction in an aerobic toluene-treating biofilter." *Biotechnology and Bioengineering*, Vol. 58, No. 4, pp.408-415.

Devinny, J.S., Deshussses, M.A., and Webster, T.S. (1999). *Biofiltration for air pollution control*. Lewis, Boca Raton, Fla.

Hershman, L. (2001). "Inoculation and Acclimation of an Autotrophic Nitrifying Carbon-Foam Based Nitric Oxide Biofilter." M.S. Project Report, University of California, Davis.

Hudepohl, N.J., Schroeder, E.D., Chang, D.P.Y. (1998). "Oxidation of Nitric Oxide in a Biofilter." Paper #98-TA20B.06, CD-ROM Proc. Air & Waste Management Association 91st Annual Meeting & Exhibition, June 14-18, San Diego, California.

Kinney, K.A., Wright, W., Chang, D.P.Y, and Schroeder, E.D. (1998). "Biodegradation of vapor phase contaminants." *Bioremediation: Principles and practice*. S. K. Sikdar and R. L. Irvine, eds., Vol. 1, Technomic Publishing Co., Lancaster, Pa., 601-632.

Lee, B., Apel, W., and Smith, W. (1999). "Effect of Oxygen on Thermophillic Denitrifying Populations in Biofilters Treating Nitric Oxide Containing Off-Gas Streams". Paper #99-322,

CD-ROM Proc. Air and Waste Management Association 92nd Annual Meeting & Exhibition, St. Louis, Missouri, June 20-24.

Mansell, B.O., Vellis, L.D., and Schroeder, E.D. (2000). "Automated Separation and Conductimetric Determination of Inorganic Nitrogen." *Journal of Environmental Engineering*. 126(8): 778-780.

Nascimento, D. (2000). "Utilizing an Autotrophic Biofilter for Oxidation of Nitric Oxide in a Combustion Off-Gas." Thesis, University of California, Davis.

Onda K., H. Takeuchi, Y. Okumoto (1960). "Mass transfer coefficients between gas and liquid phases in packed column." *Journal of Chemical Engineering of Japan* Vol. 1(1):56-62.

Ottengraf, S.P.P. (1986). "Exhaust Gas Purification." In *Biotechnology*, Rehm, H.J., Reed, G., Eds., VCH Verlagsgesellschaft, Weinheim, Germany, Vol. 8, pp 425-452.

Pogrebnaya, V.L.,Usov, A.P., Baranov, A.V., Nesterenko, A.I., (1975). *Journal of Applied Chemistry.* USSR 48, 1004.

Rasmussen, R.A., and Khalil, M.A.K. (1986). "Atmospheric Trace Gases: Trends and Distributions Over the Last Decade." *Science*, 232:1623-1624.

Woertz, J. R., Kinney, K. A., McIntosh, N. D., Szaniszlo, P. P. J. (1999). "Removal of Nitric Oxide in a Fungal Vapor-Phase Bioreactor." Paper #99-297, CD-ROM Proc. Air & Waste Management Association's 92nd Annual Meeting & Exhibition, St. Louis, Missouri, June 20-24.

Wink, D.A., Darbyshire, J.F., Nims, R.W., Saavedra, J.E., Ford, P.C., (1993). *Chemical Resource Toxicology.* Vol. 6, 23-27.